Silver metalized mixed phase manganese-doped titania: Variation of electric field and band bending within the space charge region with respect to the silver content

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1. Introduction

Heterogeneous photocatalysis is a photon activation process intended for the efficient utilization of photon energy. Efforts are made to use the solar energy efficiently. In this regard, the materials being developed are required to possess good efficiency in photon absorption, which in turn leads to the generation of the electron–hole pairs. If the lifetime of the photogenerated charge carriers is increased, they can also be efficiently utilized in oxidation and reduction processes. Among the semiconductors employed, TiO₂ is most widely used because of its suitable flat band potential, chemical state, non-toxicity, strong oxidation capacity and also its high photocatalytic activity. However, the use of TiO₂ is impaired by its wide band gap (≈3.2 eV), which requires UV light for photocatalysis, and its major limitation is the higher recombination rate of the photogenerated charge carriers resulting in lower quantum yield [2–8]. In this regard, our research group had previously reported the incorporation of the paramagnetic Mn²⁺ ions in anatase lattice at Ti⁴⁺ substitution site [9]. At lower Mn dopant concentration (<0.02%), the catalyst exhibits only anatase phase. With an increase in the dopant concentration from 0.02% to 0.06%, rutile phase starts appearing in the catalyst and the phase content of anatase to rutile is found to be in the ratio of 90:10. But at still higher dopant concentration, the phase content ratio changes to 52:48. The photocatalyst with 0.06% Mn showing bicrystalline framework of anatase and rutile had shown higher efficiency compared to all the other catalysts, which had either only anatase phase or mixed phase in different ratios. The synergistic effect between the two pairs of polymorphs is maximum for 0.06% manganese dopant concentration, and hence the optimum concentration of manganese was found to be 0.06% for efficient photocatalytic activity. This catalyst Ti₁₋₀.₀₆Mn₀.₀₆O₂ was chosen for the Ag metal deposition in the present study. It is abbreviated as Mn–TiO₂. Incorporation of Mn²⁺ ions into the TiO₂ lattice had immense influence on electronic, optical and catalytic properties. Further doping of Mn²⁺ ion in TiO₂ lattice resulted in partial phase transformation from anatase to rutile and the phase transformation temperature was reduced by 100 °C [9]. The enhanced activity of this catalyst was attributed to the synergistic effect of bicrystalline framework of anatase and rutile, small crystallite size and high intimate contact between the...
crystallites of both the phases. In the present research work an attempt has been made to increase the life time of the photogenerated charge carriers by the deposition of nano Ag metal particles on the surface of Mn–TiO₂, and these metal depositions act as efficient electron acceptors and thereby hinder the recombination of photogenerated charge carriers. Silver is preferred since it is relatively affordable compared to the other noble metals. Ag possesses bactericidal property and it also possesses preferential oxygen adsorption quality [10–15]. The thickness of the depletion layer and space charge region is influenced by the size of the deposited metal nanoparticles and hence the present research attempts an elaborate study on the mechanism of an interfacial electron transfer at the heterojunctions. This research study aimed to understand the various governing factors in this regard which influence the photocatalytic efficiency of surface metal deposited mixed phase titania [16]. Silver was deposited on the surface of Mn–TiO₂ by photo induced deposition method and the percentage of silver was varied from 0.10 to 1.5%. The variation in the thickness of the space charge region, depletion layer, accumulation layer and the extent of band bending is elaborately discussed with the variation of silver content on the surface of the catalyst. The photocatalytic activities of all the catalysts were evaluated by using resorcinol (Rs) as model compound in the presence of UV and solar light illumination. Further the efficiency of photodegradation reaction was evaluated in the presence of electron acceptors such as hydrogen peroxide (HP) and ammonium persulphate (APS). All the samples were characterized using powder X-ray diffraction (PXRD), UV–visible (UV–vis) absorbance spectroscopy, Fourier transform infrared (FTIR) spectroscopy, photoluminescence (PL), scanning electron microscope (SEM) and transmission electron microscopic (TEM) techniques.

2. Experimental

2.1. Materials

Titanium (IV) chloride (TiCl₄ ≥ 99.9%) was obtained from Merck Chemicals Limited. Resorcinol, sodium hydroxide (NaOH), sulphuric acid (H₂SO₄), ammonium persulphate (APS), hydrogen peroxides (HP) (30%, w/v) and AgNO₃ were from Sisco-Chemical Industries, Bombay. All the reagents used were of analytical grade. Double distilled water was used throughout the experiment.

2.2. Catalyst preparation

Anatase TiO₂ was prepared by sol–gel method (SG-TiO₂) through the hydrolysis of TiCl₄ as reported earlier [17]. Ag deposition on the surface of the photocatalyst was carried out by photoreduction of AgNO₃ in the presence of oxalic acid in an aqueous suspension as prepared by Szabo-Bardos et al. [15,18]. Silver loading was varied from 0.10 to 1.50% on the surface of the photocatalyst by varying the concentration of silver nitrate. An aqueous solution of AgNO₃ (1.24 × 10⁻⁴) and oxalic acid (5 × 10⁻³ M) along with Mn–TiO₂ (1 g) was suspended in 1 L of distilled water and was stirred vigorously under UV irradiation for 40–50 min to get 0.1% of silver deposit. Silver deposited samples were designated as MnTiO₂/Ag(X), where X is the Ag percentage and is equal to 0.1, 0.5, 1.0 and 1.5%. The pH of the suspension was adjusted to 6.8–7.0 by the addition of 0.1 N NaOH solution. After the irradiation the solution containing Mn–TiO₂/Ag(X) was then allowed to stand for 6 h. Depending on the percentage of deposited silver the color of the photocatalyst changed from pale rose to dark brown indicating the reduction of Ag⁺ to Ag⁰ and confirming the deposition of Ag⁰ on the surface of TiO₂. The solid was filtered, washed, dried and then heated at 120 °C for 2 h. The absence of silver in the aliquot sample of reaction mixture confirms the complete deposition of Ag metal on the semiconductor particle surface.

2.3. Characterization of the catalyst

The PXRD patterns of samples were studied using Philips PW/1050/70/76, X-ray diffractometer was operated at 30 kV and 20 mA. Cu Kα is used as a source with nickel filter at a scan rate of 2°/min. FTIR spectra (NICOLLET IMPACT 400D FTIR spectrometer) of all the samples were studied in the range of 400–4500 cm⁻¹ using potassium bromide as reference. The diffuse reflectance spectra (DRS) of all the photocatalyst samples in the wavelength range of 300–500 nm were obtained using a UV Vis (31031 PC) near-IR spectrophotometer with BaSO₄ as reference standard. Photoluminescence (PL) spectra of the generated 2-hydroxynaphthalic acid were measured on a Hitachi F-7000 fluorescence spectrophotometer. The band gap values (E⁰) of all the photocatalysts were calculated by using Kubelka–Munk plot. Surface morphology was analyzed by SEM analysis using JSM840 microscope operating at 25 kV on specimen upon which a thin layer of gold had been evaporated. An electron microscope is used in the EDX mode. Transmission electron microscope (TEM) images were recorded using Philips CM200 operated at 200 kV. The residual concentration of the Rs during the degradation process was measured by using UV–vis spectrophotometer (Shimadzu UV-1700 Pharmaspec) in the region of maximum absorption (190–600 nm).

2.4. Photochemical reactor

Experiments were carried out at room temperature using a circular glass reactor whose exposure surface area was found to be 176.6 cm². A 125 W medium pressure mercury vapor lamp was used as the UV light source. Photon flux was found to be 7.84 mW/cm² by ferrooxalate actinometry. The wavelengths of the light peaks were around 370 nm. The reaction mixture was stirred continuously and exposed to UV irradiation directly by focusing the light at a distance of 29 cm. All the experiments were performed using double distilled water. Solar light experiments were performed under sunlight between 11 am and 2 pm when the solar intensity fluctuations were minimum. The experiments were conducted in the months of April–May at Bangalore, India. The latitude and longitude of the place are 12.58 N and 77.38 E respectively. The average solar light intensity was found to be 0.767 kW m⁻² (using solar radiometer). The reaction mixture was exposed to the sunlight by focusing through convex lens. The solar radiation as a function of wavelength was measured by photometer, which shows a maximum at 450 nm. Photocatalytic activities of all the photocatalysts were evaluated simultaneously, in order to minimize the errors due to fluctuations in solar intensity. A typical experiment contains 100 mg of the photocatalyst in 250 mL of 10 ppm Rs solution (along with 20 ppm of APS or 10 ppm of hydrogen peroxide when required). The reaction mixture was stirred constantly throughout the experiment. The samples were centrifuged and filtered through 0.45 μm Millipore filter to remove the catalyst particles, and the centrifugate containing residual Rs was analyzed by UV–vis spectrophotometric technique in the wavelength range of 190–600 nm.

3. Results and discussions

3.1. Powder X-ray diffraction (PXRD) studies

S1 shows the PXRD patterns of SG-TiO₂, Mn–TiO₂/Ag (0.1%), Mn–TiO₂/Ag (0.5%), Mn–TiO₂/Ag (1.0%), and Mn–TiO₂/Ag (1.5%) photocatalysts. Detailed characterization data corresponding to Mn–TiO₂ have been reported elsewhere [9]. All the photocatalysts show PXRD peaks corresponding to anatase phase at 2θ values of
Table 1
Summary of data obtained by X-ray diffraction, UV–vis absorption and reflectance techniques. D: crystallite size in nm, λ: lattice parameters, (A)1: unit cell volume, λmax: absorption maxima in nm, and Eg: band gap energies in eV.

<table>
<thead>
<tr>
<th>Photo catalysts</th>
<th>D (nm)</th>
<th>(A)1</th>
<th>λmax (nm)</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG-TiO2</td>
<td>31.94</td>
<td>3.7908</td>
<td>136.74</td>
<td>381.47</td>
</tr>
<tr>
<td>Mn–TiO2/Ag (0.1%)</td>
<td>26.62</td>
<td>3.7936</td>
<td>136.14</td>
<td>455.62</td>
</tr>
<tr>
<td>Mn–TiO2/Ag (0.5%)</td>
<td>21.79</td>
<td>3.7936</td>
<td>135.66</td>
<td>455.07</td>
</tr>
<tr>
<td>Mn–TiO2/Ag (1.0%)</td>
<td>23.65</td>
<td>3.8058</td>
<td>139.26</td>
<td>454.87</td>
</tr>
<tr>
<td>Mn–TiO2/Ag (1.5%)</td>
<td>25.23</td>
<td>3.8000</td>
<td>137.28</td>
<td>455.67</td>
</tr>
</tbody>
</table>

3.2. UV–vis absorbance and DRS studies

TiO2 shows maximum absorption peak at 380 nm and the absorption band in the UV region is due to the electronic transition from O 2p valence band (VB) to Ti 3d conduction band (CB). UV–vis absorbance and reflectance spectra of SG–TiO2, Mn–TiO2/Ag (0.1%), Mn–TiO2/Ag (0.5%), Mn–TiO2/Ag (1.0%), and Mn–TiO2/Ag (1.5%) photocatalysts are shown in S2a and S2b respectively. All the Mn–TiO2/Ag (X) samples show slight shift in the absorption peak to the higher wavelength region and it shows continuous absorption tailing in the visible region, which can be attributed to the plasmon effect by silver particles and manganese doping. The band gap energies were calculated from DRS data by using Kubelka–Munk plot of $(1-R^2)2/4R_c$ versus wavelength, where $R_c$ is the ratio of relative reflected intensity of the sample to that of nonabsorbing standard BaSO4 (Table 1) [15]. The optical band edge of the Mn–TiO2/Ag(X) shows a remarkable red shift toward the visible region compared to that of SG–TiO2. The absorption maximum corresponding to the intrinsic and extrinsic band gap values of all the photocatalysts is summarized in Table 1. SG–TiO2 shows optical absorption threshold at ~380 nm which corresponds to the band gap of 3.25 eV (inset of S2). Mn–TiO2/Ag (0.1%) shows maximum absorption peak at 455.62 nm corresponding to the indirect band gap of 2.72 eV, and the intensity of this absorption peak is high compared to that of all the other photocatalysts. The $\lambda_{max}$ and $E_g$ values of all the samples are shown in Table 1.

3.3. FTIR analysis

FTIR spectra of SG–TiO2, Mn–TiO2/Ag (0.1%), Mn–TiO2/Ag (0.5%), Mn–TiO2/Ag (1.0%) and Mn–TiO2/Ag (1.5%) photocatalysts in the range of 400–4000 cm$^{-1}$ were analyzed and are shown in S3. The spectra show roughly similar band at ~1630 cm$^{-1}$ attributed to the OH bending vibration of chemoisorbed or physisorbed H2O molecule on the photocatalyst surface of all the samples [19]. The intensity of this peak is higher for Mn–TiO2/Ag (0.1%) compared to SG–TiO2. Further this peak intensity decreases slightly with increase in the concentration of the metallic silver on the surface of TiO2. The peaks at ~3400, 2930 and 2850 cm$^{-1}$ were attributed to the Ti–OH bond in the case of SG–TiO2 [20]. The FTIR spectrum of TiO2 exhibits strong absorption band at ~466 cm$^{-1}$, which may be due to the vibrations of Ti$^3$O$^-$–Ti, Ti$^3$O$^-$–O and Ti$^3$O$^-$ bonds in the TiO2 lattice. The Ti$^3$O–Ti bands are observed in the frequency range of 500–900 cm$^{-1}$ [21,22]. The peak at ~2360 cm$^{-1}$ is observed only for SG–TiO2 and Mn–TiO2/Ag (1.5%) and is due to the adsorbed H2O molecules. The hydroxyl groups present on the surface of SG–TiO2 and Mn–TiO2/Ag (1.5%) show a broad band due to the deformation vibrations ~3450–3550 cm$^{-1}$ and the intensity of these bands are low for the other manganese-doped titanates.

3.4. PL analysis

The processes of the charge carrier trapping, transfer and migration of photogenerated electron–hole pairs in semiconducting photocatalysts are investigated using PL emission spectra. The peak in the spectrum arises due to the recombination of the free charge carriers [15,23–27]. Many binding states exist between CB and VB which are created due to the presence of defects such as oxygen vacancies, surface states and other impurities like dopant [28]. Some of the photogenerated electrons can be trapped by these surface defects and oxygen vacancies leading to the formation of excitons within these states which is thermodynamically more favorable compared to the conduction band trapping [29]. When the excitons return to VB, photons are released producing PL signals. S4 shows the PL spectra of SG–TiO2, Mn–TiO2/Ag (0.1%), Mn–TiO2/Ag (0.5%), Mn–TiO2/Ag (1.0%), and Mn–TiO2/Ag (1.5%) photocatalysts. PL intensities of these samples decrease in the following order: SG–TiO2, Mn–TiO2/Ag (1.5%) > Mn–TiO2/Ag (1.0%) > Mn–TiO2/Ag (0.5%) > Mn–TiO2/Ag (0.1%). The peak around 430 nm originates from the bound excitation emission due to the trapping of free excitons by TiO2 octahedra close to the defects. Further the spectra show that doping of Mn has remarkable effect on the emission peak intensity. This peak intensity is low for Mn–TiO2/Ag (0.1%) and it is found to be high for SG–TiO2. With increase in the silver content the peak intensity increases, implying the higher rate of recombination of charge carriers. Alternatively the peak at 430 nm may also arise from radiative annihilation of excitons and it is a band to band recombination, while the peak at 530 nm is attributed to electron transition mediated by defect levels such as oxygen vacancies or surface states in the band gap [29,30]. The intensity of the peak in the PL spectra gives a measure of the rate of recombination of electrons and holes in the semiconductor. PL intensities of both the peaks are lower for Mn–TiO2/Ag (0.1%) photocatalyst. This can be accounted for the lower rate of recombination of electrons and holes. The optimum silver content on the surface of manganese-doped titanate efficiently traps the photoinduced electrons and acts as a charge separator, thereby increasing the life time of electron and holes. A Schottky barrier is formed at the metal–semiconductor interface. The PL intensities of both the above peaks are higher for SG–TiO2 and lower for Mn–TiO2/Ag (0.1%) compared to that of all the other photocatalysts (SA4 and S4b).

3.5. SEM and EDX analysis

Surface morphologies of all the samples were analyzed by using SEM analysis and are as shown in Fig. 1a–e. SEM images show significant difference in the morphologies of SG–TiO2, Mn–TiO2/Ag (0.1%), Mn–TiO2/Ag (0.5%), Mn–TiO2/Ag (1.0%) and Mn–TiO2/Ag (1.5%) photocatalysts. EDAX spectra of SG–TiO2 and Mn–TiO2/Ag (0.1%) are shown in Fig. 1f and g. Atom percentages of oxygen, titanium, manganese and silver were found to be 51.21, 48.61, 0.08 and 0.10% respectively for Mn–TiO2/Ag (0.1%) sample. Similar atom percentages of oxygen and titanium in SG–TiO2 were found to be around 50.39 and 49.61% respectively.

Please cite this article in press as: B. Nagaraj, L.G. Devi, J. Mol. Catal. A: Chem. (2014), http://dx.doi.org/10.1016/j.molcata.2014.03.019
EDAX analysis confirmed the presence of deposited silver particles on the surface of Mn–TiO₂ (Fig. 1g).

3.6. XPS analysis

XPS is used to investigate the elemental state and chemical composition of the surfaces of all the photocatalysts. XPS of Mn–TiO₂/Ag (0.1%) sample is given in Fig. 2.

The deposition of silver on the surface of TiO₂ was confirmed by the presence of Ag 3d peaks. The binding energy peaks corresponding to Ag 3d appear at 367.7 and 373.7 eV. The peak separation in this case was found to be 6.0 eV which corresponds to the Ag⁰ metallic state (Fig. 2d). The data obtained exhibit a negative shift compared to that expected for bulk Ag at 368.3 eV for 3d_{5/2} and 374.3 eV for 3d_{3/2} values. The observed change is due to the increase in the outer electron cloud density of deposited Ag particles [31–33]. The shift in the binding energies is probably due to the transfer of some of the conduction band electrons from the bulk of Mn–TiO₂ to the surface Ag particles. The concentration of Ag from XPS studies was found to be 0.12 atom percent. To further confirm the interactions between the silver nanoparticles and TiO₂, the chemical states of Ti were examined by this technique.

Fig. 1. SEM images of (a) SG-TiO₂, (b) Mn–TiO₂/Ag (0.1%), (c) Mn–TiO₂/Ag (0.5%), (d) Mn–TiO₂/Ag (1.0%) and (e) Mn–TiO₂/Ag (1.5%). EDAX of (f) SG-TiO₂ and (g) Mn–TiO₂/Ag (0.1%).
Fig. 2. Wide scan XPS spectra of Mn–TiO$_2$/Ag (0.10%), (a) Ti 2p, (b) O 1s, (c) Mn 2p and (d) Ag 3d core level XPS spectra of Mn–TiO$_2$/Ag (0.10%).

The binding energy peak positions of Ti 2p$_{1/2}$ are found at 457.5, 455.3 and 456.3 eV and Ti 2p$_{3/2}$ is observed at 462.2 eV. Curve fitting the data shows a peak at 457.5 eV due to Ti$^{4+}$, 456.3 eV due to Ti$^{3+}$ and 455.3 eV attributed to Ti$^{2+}$ in Ti 2p data as shown in Fig. 2a [34]. The increase in the effective negative charge on element leads to the decrease in the binding energy of Ti 2p electrons, indicating an increase in the average electron density on the titanium, and it is a direct measure of the lowering of valence state of Ti$^{4+}$. The partial reduction of Ti$^{4+} \rightarrow$ Ti$^{3+}$ and Ti$^{3+} \rightarrow$ Ti$^{2+}$ leads to the decrease in the binding energy of Ti 2p values [35–37]. The shoulder peaks around 456.2–456.7 eV is attributed to Ti$^{2+}$ in the Ti 2p$_{3/2}$ spectrum [34]. The XPS spectrum of O 1s region shows major
peak around 529.1 eV corresponding to the Ti–OH metal hydroxide bond (Fig. 2b) [38]. The Mn 2p_3/2 and Mn 2p_1/2 show the binding energy peaks at 640.8 eV and 653.1 eV respectively. These peaks with energy separation around 12.3 eV can be assigned to the Mn^{2+} ion [39]. The shift in binding energies around 0.2 eV indicates that the electron density around Mn has decreased in the TiO_2 lattice, which may be due to interaction of Mn^{2+} ions with the titanium ions as shown in Fig. 2c.

3.7. Transmission electron microscopic (TEM) analysis

The crystallite size and distribution of the particles in the TiO_2 (Fig. 3a and b) and Mn/TiO_2/Ag (0.10%) (Fig. 3d and e) catalysts were investigated by the TEM analysis. The average size of the anatase TiO_2 nanocrystals was found to be 34.26 nm, which is in agreement with the calculated XRD data. The average perimeter, thickness, length and inner diameter of the TiO_2 particles were found to be 26.78 nm, 3.54 nm, 9.86 nm, 52.15 nm respectively.

The electron diffraction patterns of the TiO_2 and Mn–TiO_2/Ag (0.10%) particles are shown in Fig. 3c and f. The interplanar distances of both the catalysts are in agreement with the calculated XRD data. Fig. 3d and e shows the TEM micrograph of the Mn–TiO_2/Ag (0.10%) catalyst. The average particle size distributions in Mn–TiO_2/Ag (0.10%) were found to be 48.25 nm. The average perimeter, thickness, length and inner diameter of the Mn–TiO_2/Ag (0.10%) particles were found to be 42.14 nm, 4.15 nm, 33.10 nm, and 56.86 nm respectively. The average sizes of silver particles were found to be in the range of approximately 14–22 nm.

3.8. Metal/semiconductor contact induced band bending due to the variation of electric and potential fields in the space charge region as described by finite and infinite interface models

If the work function of the metal (φ_m) is higher than that of the semiconductor (φ_s), φ_m > φ_s, then the electrons will flow from the semiconductor to the metal. This transfer of the electrons will occur up to the point of equalization of Fermi levels of the metal and semiconductor. At the metal/semiconductor interface the metal is negatively charged and the semiconductor is positively charged due to electrostatic induction. Since the concentration of the free charge carriers is low in the semiconductor, the electric field between the metal and semiconductor interface cannot be effectively screened in the semiconductor. Hence the free charge carriers on the surface of the semiconductor are depleted compared with the bulk and this region is known as the space charge region. The band edge positions in the space charge region of semiconductor are continuously shifted due to the variation in the electric field between the semiconductor and metal arising due to the charge transfer. This makes the semiconductor band edges to bend and it is referred to as band bending (V_BB). When φ_m > φ_s the energy bands bend upwards at the interface, and when φ_m < φ_s the energy bands bend downwards. The work function difference between the metal and the semiconductor influences the degree of V_BB at the interface [16,40–43].

\[ V_{BB} = \phi_m - \phi_s \]  
(1)

The work function of the metallic silver φ_m varies from 4.3 to 4.7 and the work function of TiO_2 semiconductor φ_s is approximately 4.3. The V_BB value is found to be 0.4 eV (for φ_m = 4.7 eV and φ_s = 4.3 eV). The height of Schottky barrier (φ_SB) formed at the metal–semiconductor interface is given by

\[ \phi_{SB} = (\phi_m - \chi_s) = 0.6 \text{ eV} \]  
(2)

\[ X_s \] is the electron affinity of the semiconductor (4.1 eV) and the value of φ_SB will vary from 0.2 to 0.6 eV [44]. The free charge carrier density is of the order ~10^{17} and ~10^{22} cm^{-3} for semiconductor and metal respectively. This difference in the charge densities creates a space charge region whose thickness is in the order of ~100 Å. Physical and chemical properties such as energy band structure, local conductivity and free charge carrier density will have different values within the bulk region and the space charge region [45]. The charge transferred per unit area from the semiconductor to metal is given by Q and the equation can be represented as

\[ Q = \sum \text{e} \text{N}_s \]  

Assuming the values of donor density \text{N}_d = 10^{15} \text{cm}^{-3}, relative dielectric constant \varepsilon_r of the semiconductor and the vacuum permittivity \varepsilon_0, values are 75 F/m (between 1 and 100 KHz) and 8.854 \times 10^{-12} F/m respectively [46]. The value of Q was found to be 4.4833 \times 10^{-26} C. Since V_BB is a one-dimensional quantity, which is the function of distance from the surface into the bulk, the value of this quantity can be taken along z direction alone. The depletion layer thickness (D) can be obtained by the following equation:

\[ D = \sqrt{\frac{2\varepsilon_r \varepsilon_0 V_{BB}(0)}{\varepsilon_d}} = 3.2697 \times 10^{-10} \text{ F m}^{-3}. \]

The infinite metal/semiconductor interface model can be applied when lateral width of metal/semiconductor interface is higher than the thickness of the space charge region (10 nm). However in a catalytic system where semiconductor particles with small metal deposits are used as a catalyst which are smaller than 10 nm, finite metal/semiconductor interface model is more relevant [16,47]. In this regard loannides and Verykios have proposed a model based on Schottky approximation. According to them the electric field E(r) and potential V_BB(r) in the space charge region can be calculated in the following way:

\[ E(r) = \frac{eN_d}{4\varepsilon_r \varepsilon_0 r^2} \left[ \frac{(D + r_m)^2}{2} - r^2 - \frac{(D + r_m)^3}{3r} \right] \text{ where } r_m \ll r \ll D + r_m \]  
(3)

where r is the distance from the metal particle to the semiconductor which is approximately around 26 nm and r_m is the radius of the metal particle (obtained from the computer analysis of the data obtained from TEM). The variation in electric field with respect to the radius of the Ag metal is shown in Fig. 4a. As the size of Ag metal deposit increases the magnitude of the electric field decreases. The extent of variation of the potential field V_BB (r) versus radius r and V_BB (r_m) versus r_m is given by Eqs. (4) and (5) respectively. Since r_m is a more accessible quantity for calculations, a plot of V_BB (r_m) versus r_m is shown in Fig. 4b.

The band bending potential exhibits a parabolic relationship with r_m

\[ V_{BB}(r) = \frac{eN_d}{4\varepsilon_r \varepsilon_0} \left[ \frac{(D + r_m)^2}{2} - r^2 - \frac{(D + r_m)^3}{3r} \right] \text{ where } r_m \ll r \ll D + r_m \]  
(4)

\[ V_{BB}(r_m) = \frac{eN_d}{4\varepsilon_r \varepsilon_0} \left[ \frac{(D + r_m)^2}{2} - \frac{r_m^2}{6} - \frac{(D + r_m)^3}{3r_m^3} \right] \]  
(5)

Saturation adsorption coverage on semiconductor surface by the donor or acceptor molecules will be influenced by band bending. The active defect site availability and adsorbate–adsorbent interaction on the semiconductor surface influence the extent of adsorption. The extent of band bending and the thickness of the depletion layer are influenced by the adsorption of molecules on the semiconductor surface. Assuming N_DD = N_s (the charge on the n-type dopant in depletion layer has been transferred to the
Fig. 3. TEM micrographs of (a) TiO₂ particles, (b) TiO₂ particles (high resolution), (c) electron diffraction pattern of TiO₂ catalyst, (d) Mn–TiO₂/Ag (0.10%) particles, (e) Mn–TiO₂/Ag (0.10%) particles (high resolution), and (f) electron diffraction pattern of Mn–TiO₂/Ag (0.10%) catalyst.

Fig. 4. (a) Variation of electric field $E(r)$ within the space charge region versus the radius of Ag metal deposit, (b) variation of potential field $V_{BB}(r_m)$ within the space charge region versus the radius of Ag metal deposit and (c) variation of the number of adsorbed molecules on surface (Ns) versus the radius of Ag metal deposit.
adsorbed molecule), then the equation can be modified and written as:

$$ V_{BB} = \frac{eN_D D^2}{2\varepsilon_0} = \frac{eN_Q^2}{2N_M D^2\varepsilon_0} \quad (6) $$

From Fig. 4c it can be inferred that when the radius of the deposited Ag metal particle on the surface of semiconductor is around 8 nm, the number of surface adsorbed molecules is high. The number of adsorbed molecules on the surface decreases with the increase in the size of the metal deposit.

3.9. Photodegradation of Rs

The photocatalytic activities of SG-TiO2, Mn–TiO2, Mn–TiO2/Ag (0.1%), Mn–TiO2/Ag (0.5%), Mn–TiO2/Ag (1.0%), and Mn–TiO2/Ag (1.5%) were evaluated in the presence of UV/solar light illumination for the time duration of 1.5 h. Higher photocatalytic activity is exhibited by Mn–TiO2/Ag (0.1%) under solar light illumination, which shows 97.5% degradation. SG-TiO2 (78.6%) and Mn–TiO2 (64.18%) show better activity under UV light illumination (Table 2). With further increase in the silver content above 0.10%, more number of photoinduced electrons are trapped by the metallic silver deposits generating space charge region with higher negative charges, which increases the probability of the hole capture by these negative charges and the recombination process dominates, thereby decreasing the efficiency of the degradation process. Further as the silver content increases on the surface of the photocatalyst, the surface area available for photon absorption decreases thereby decreasing the rate of photogeneration of electron–hole pair. The photocatalytic activity decreases with increase in the silver content above the optimum level [48,49]. Addition of the electron acceptors such as HP and APS to the reaction mixture is one of the strategies employed to decrease the rate of electron–hole recombination process. The effect of these electron acceptors is more prominent under UV-illumination. These electron acceptors are chemisorbed on the surface of the catalyst, facilitating the inelastic transfer of the electrons from CB to the oxidants. These electron acceptors can also increase the extent of generation of the free radicals and other oxidizing species. The redox potential of sulfate radical generated from APS is around 2.6 eV, which is one of the strongest oxidizing species in aqueous solution compared to hydroxyl radical (2.8 eV). The electron acceptors in the reaction mixture can accelerate the process of the electron transfer and decrease the electron–hole recombination rate. The oxidation potential of HP and S2O82− is found to be at 1.8 and 2.1 eV respectively and they are more close to TiO2 VB. The Fermi energy and the Mn2+ dopant level in TiO2 is around 0.3 and 0.53 eV below the CB respectively. The Fermi energy of metallic silver varies with the size of the metal deposit and also with the number of electrons transferred from TiO2 CB. Since the potentials of the added oxidants are more favorable for the capture of photogenerated electron, the efficiency of the degradation process increases under UV light illumination. The reaction mechanisms involving the production of these free radicals are given elsewhere [15,50–53]. However, APS did not facilitate the photodegradation process under solar light illumination. Mn–TiO2/Ag (0.1%) along with optimum concentrations of HP (10 ppm) shows maximum efficiency under solar light irradiation. The above mechanisms are more facilitated due to the presence of dopant having stable half-filled electronic configurations. The concentrations of photogenerated hydroxyl and superoxide radicals are optimum for 0.06% dopant concentration. Yu et al. have reported a method to find the concentration of hydroxyl radicals on the catalyst surface by photoluminescence studies [27]. However presently the prominent role played by the hydroxyl radicals is confirmed by conducting the photodegradation experiment in the presence of methanol, which acts as hydroxyl radical scavenger. The rate constant for the degradation reaction decreases drastically in the presence of methanol, confirming the positive role played by the hydroxyl radicals.

3.10. Charge transfer mechanism in bicrystalline framework of anatase and rutile along with plasmonic effect

The enhanced photocatalytic activity of Mn–TiO2/Ag (0.1%) can be accounted in the following way: The heterojunctions formed between mixed phase of anatase and rutile of the same semiconductor significantly reduce the rate of recombination of the photoinduced electrons and holes. The band edge positions of bicrystalline TiO2 vary slightly for different phases and the interface formed between the mixed phase acts as a good charge separator. The flat band potential of anatase and rutile was found to be −0.9 and −0.7 V (versus normal hydrogen electrode at pH 7) respectively [54]. The CB edge position of anatase is found to be slightly higher compared to that of the rutile phase [55,56]. The work function of the rutile is slightly lower than that of anatase, which causes the energy bands of rutile to bend upwards and energy bands of anatase to bend downwards [16,57]. The established electric fields near the interface makes the electrons move downhill and holes move uphill. The maximum interfacial contact between the two phases is due to their similarity in their crystallite sizes, which enhances the efficiency of the degradation process as described earlier [9]. The Mn2+ dopant has a stable half-filled electronic configuration and hence acts as a shallow electron/hole trap, which means it can trap and detraps the charge carriers more easily to obtain its stable half-filled electronic configuration. If Mn2+ traps a hole, the hole is transferred more easily to hydroxyl anion, producing hydroxyl radicals to attain the stable half-filled electronic configuration [9,58]. When the catalyst is excited under UV irradiation, the anatase phase absorbs the photons and the photoinduced electrons are excited to the CB. Some of the electrons are trapped by the silver deposits and the remaining electrons are transferred to the CB of rutile phase, which is around 0.2 eV below the CB of anatase phase and hence results in better charge separation. In case of solar light illumination, the band gap of rutile is more suitable for absorption. Some of the photoinduced electrons are trapped by the silver deposits and the remaining electrons are transferred to the electronic trapping sites or to the dopant impurity level (which is 0.5 eV below the CB edge of anatase phase) or to the lattice trapping sites (which is around 0.8 eV below the CB edge of anatase) of anatase phase [9,59,60]. In presence of solar light illumination the plasmonic silver nanoparticles deposited on the TiO2 surface are efficient at scattering and absorbing solar light. Deposited Ag particles are excited and the electrons on the metal surface undergo collective oscillation known as the surface plasmon resonance effect (SPR). Due to these oscillations, there is an enhancement of the electric near-field on the silver particle surface and all around silver nanoparticles. As a result the electrons are transferred from the VB to the CB of Mn–TiO2/Ag (0.1%) under solar light irradiation. The electric near-field of the deposited silver particles increases the life span of the electron–hole pair and reduces the recombination process [61–63]. The metallic Ag deposit on both anatase and rutile phases plays a crucial role in enhancing the separation of photogenerated charge carriers and increases the efficiency of the photocatalyst. The charge transfer process at the interface of Ag and TiO2 contact creates Schottky barrier owing to the differences in the work function of Ag and TiO2. This barrier mainly traps the electrons thereby reducing the rate of recombination of electrons and holes [32,64]. This mainly increases the concentration of holes in the VB of both anatase and rutile. These holes from VB can react with the water or the hydroxyl ions forming hydroxyl radicals. The band bending may influence the photochemistry of a semiconductor in three different ways: (i) the band bending can influence thermal
adsorption and desorption of Rs, (ii) the extent of band bending can also influence photoreaction process by modulating photoexcited charge carrier transfer and recombination process and (iii) the model proposed by Weisz suggests that the adsorption coverage of donor and acceptor molecules on the semiconductor surface will also be influenced by the band bending [65]. In addition adsorption is also influenced by the number and nature of defect sites and adsorbate–adsorbent interactions on a semiconductor surface.

3.1.1. Comparison of photocatalytic activity of silver deposited catalyst

The optimum Ag deposition is found to be 0.10% and with further increase in the silver content, the efficiency of the photoreaction decreases (Fig. 5). This could be attributed to the following reasons: the magnitude of electric field decreases with increase in the percentage deposition of Ag metal.

Band bending potential increases with Ag metal clusters and the number of adsorbed molecules on the surface of TiO2 decreases with increase in the percentage of deposited Ag metal particles.

4. Conclusion

The observed higher photocatalytic activity of Mn–TiO2/Ag (0.10%) photocatalyst can be accounted in the following way:

• The potential difference in the energy levels of CB and VB in bccrystalline framework of anatase and rutile mixed phase catalyst leads to the formation of the interface at the heterojunction which acts as a good charge separator.

• The work function of anatase and rutile phases in the mixed phase titania is different and hence energy bands of anatase bend downwards, whereas the energy bands of rutile bend upwards. This band bending leads to the migration of the electrons and holes at the heterojunctions in mixed phase photocatalyst, which decreases the recombination rate of electron–hole pairs.

• The ratio of the phase content (anatase to rutile) in the bccrystalline framework as well as the maximum interfacial contact due to their similarity in crystal sizes plays a major significant role in enhancing the efficiency.

• Dimensional size of deposited Ag particles plays a significant role in enhancing the photocatalytic activity. Depending on the size of the silver deposit, the energy level of silver varies from −4.64 to −1.30 eV (with respect to vacuum energy level).

• Energy levels of the optimized Ag particles are lower than the CB edge of TiO2 and they are in close proximity with the electron affinity of the dissolved oxygen. Hence the electrons can be trapped by the silver particles and in turn can be transferred to the oxygen molecule.

• Beyond the optimum Ag concentration (>0.10%), the space charge region within the semiconductor becomes more negative and facilitates the recombination process.

• The surface plasmon resonance frequency of the metal particles can be tuned to the visible light absorption by changing the size of the deposited metal particles on the mixed phase titania.

• The presence of binding states such as defects, oxygen vacancies and surface states with different energies in the mixed phase catalyst plays a vital role in enhancing the efficiency of the photocatalyst.

• The insertion of Mn2+ dopant with the stable half-filled electronic configuration traps and detrap the electrons and holes more readily, leading to the formation of the superoxide and hydroxyl radicals respectively.

• The heterojunctions of Ag/rutile/anatase/Ag at optimum Ag concentration enhance the photocatalytic activity.

Acknowledgements

The authors greatly acknowledge the Department of Science and Technology (DST–SERC, DST–IDP), UGC Major Research Project and Government of India for the financial assistance.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.03.019.

References